

APPENDIX C

Summary of Data Review Findings

EXECUTIVE SUMMARY

The EPA Region 4 South Florida Everglades Ecosystem Assessment Project is a pioneering research and monitoring effort to assess mercury contamination, eutrophication, habitat alteration, and hydroperiod modifications in the South Florida Everglades ecosystem using the ecological risk assessment process. Over a four year period, this Project made over 20,425 measurements on 20 constituents in 5 different media at about 200 canal stations, 550 marsh stations during the 9 field sampling events over the 10,000 km² area in South Florida. Included in these measurement were 7 structures sampled on a bi-weekly basis from February 94 thru February 97. The large scale patterns in total phosphorus and eutrophication, mercury contamination, and habitat types, observed for the first time because of this Project are described in the 1998 South Florida Ecosystem Assessment Technical Report, Volumes I and II (Stober et al., 1998). To accommodate this large sample load, and to analyze ultra-trace level concentrations of selected constituents, new methods also were developed as part of this Project. In addition to the quality assurance reviews that occurred as part of the data analysis, a rigorous quality assurance/quality control review was conducted on the data by scientists of the Region 4 Science and Ecosystem Support Division (SESD), Office of Quality Assurance (OQA).

OQA was requested to review all contractor data provided by laboratories supporting the SESD Everglades ecosystem project. Raw data were obtained from each laboratory involved and were reviewed against the four levels of criteria addressed in: 1. the Data Quality Objectives (DQOs), 2. requirements stated in Section 2.5; Data Quality Requirements in the EPA Project Research Plan, 3. the laboratories' respective Standard Operating Procedure (SOP) and 4. quality control (QC) practices, and procedures typically applied for regulatory and compliance reviews conducted by the OQA. The OQA goals were:

- to reconstruct the final reported data for the field, laboratory and QC activities,
- to determine if the contract laboratories' documentation was accurate and provided adequate defensibility of the monitoring data, and
- to verify if the data were of acceptable quality based on the Project design.

Review findings are documented in this *Summary of Data Review Findings* for each constituent by media and by cycle and applicable recommendations are included.

Quantitative and qualitative evaluations indicate the vast majority of the data were of acceptable quality, and met the overall DQOs of the Project design. All data sets will have some QA/QC deficiencies and certain QC procedures and documentation deficiencies also were noted in the Project data. Out of the over 20,425 measurements made over the four year period, only 15 percent of the data were qualified. There were 1,325 points flagged "NR"- not reviewed because raw data were not available from the laboratory, 1,783 assigned a "J" flag - analyte identification was acceptable for use but certain QC criteria were not satisfied and 256 values rejected and not reported in the database.

The data that have been qualified after this rigorous review are:

- “J” – Soil/sediment methyl mercury for the secondary laboratory
- “NR” – Water total mercury for September 1993 Canal samples and April ‘94 transect data for primary laboratory
- “J” – Water total mercury, excluding September 1993 Canal, for primary laboratory.
- “J” – Periphyton total mercury for primary laboratory
- “J” – Soil/sediment total mercury for May 1994, 1995 Canal cycles and May 1996 marsh samples for secondary laboratory
- “NR” – Soil total mercury for September 1995 marsh split samples for secondary laboratory.
- “J” – Mosquitofish total mercury for very low mercury concentration fish for primary laboratory
- “J” – Total nitrogen for the secondary laboratory for Sept. ‘96 marsh samples
- Reject – Water alkaline phosphatase activity for 123 samples for May 1996 marsh cycle from the primary laboratory
- Reject – Water sulfide for 123 samples for the September 1995 marsh cycle from the primary laboratory.

The Study was designed to have a minimum of 10 percent of the samples split for certain parameters with a second laboratory to provide between laboratory comparability and field duplicates to provide a combined field and laboratory precision. Samples for certain parameters were split at a higher frequency than 10 percent. The higher frequency of split sample data provided strong analytical support for data analysis and interpretation even though documentation or record retention may have been lacking in some cases.

The OQA finds that the data provided by all laboratories (EPA and supporting) permit assessment of trends and the characterization of the Everglades on a spatial and temporal basis and satisfy the Project objectives. Data qualified with a “J” code would not compromise the characterization and trend analysis or Project objectives. “J” coded data should not be used solely in the setting of environmental standards unless additional data are collected to substantiate these original values that has all supportive QC and documentation. These data can be used as part of the weight of evidence approach for establishing environmental standards.

This *Summary of Data Review Findings* report should be kept in perspective. The South Florida Everglades Ecosystem Assessment Project was a research and monitoring effort, not a regulatory compliance project. It developed and implemented new methods for rapidly analyzing a large sample load with ultra-trace level constituent concentrations. The QA/QC review, however, included rigorous QA/QC methods used in reviewing compliance monitoring data. Yet, out of the over 20,425 measurements made over the four year period, only 15 percent of data were qualified.. This data set should provide an important baseline for assessing the current conditions of the Everglades ecosystem and for monitoring future trends in this condition. The results from this QA/QC Review have already been, and will continue to be, used to refine the QA/QC procedures in future Project monitoring efforts.

INTRODUCTION

In 1993, EPA Region 4 Science and Ecosystem Support Division (SESD) initiated the South Florida Everglades Ecosystem Assessment Project. This pioneering 10,000 km² system wide research and monitoring project was conducted to assess mercury contamination, eutrophication, habitat alteration, and hydroperiod modification using an ecological risk assessment process. A statistical survey design was used to select 200 canal sites and 500 marsh sites to sample for 20 constituents measured in 5 different media during 4 different periods or cycles. In addition, transect sampling was conducted to test the marsh sampling procedures, constituents were measured on a bi-weekly basis at 7 structures in the South Florida system, and new methods were developed to accommodate the large sampling load and measure ultra-trace level constituent concentrations. Over a four year period, this project made over 20,425 measurements in the South Florida Everglades ecosystem.

Although QA/QC procedures were designed into the Project from its onset, a *Quality of Science Review* was requested from the EPA Office of Research and Development (ORD) National Exposure Research Laboratory (NERL) Environmental Sciences Division (ESD)—Las Vegas, in 1995. ORD was, and continues to be, in the process of trying to develop a Data Quality Objectives (DQO) process for research projects similar to the DQO process developed for regulatory and compliance programs (EPA 1994). This has proven to be a formidable task. The purposes of the NERL-ESD review were to (1) identify quality-related issues and provide recommendations for correction or improvement, and (2) to provide the project participants with the necessary tools to enable them to continue to monitor data quality. The *Quality of Science Review* report (Chaloud, Heitmar, and Birch 1996) was provided to SESD in April 1997. The *Quality of Science Review* report identified a number of strengths in the Everglades Mercury Study. Strengths of this project include:

- Project Design
- Personnel
- Field Operations
- Sampling Procedures
- Low Crew Variability
- Project Management
- Sample Representativeness
- Laboratory QA/QC Programs
- Low Error Rate in data Base
- Spatial Analyses

Recommendations suggesting positive corrective actions were commenced or implemented during the on-site audits in 1995 and continued during successive sampling events and data evaluation by the OQA and the laboratories involved. Three areas were specifically mentioned in the *Review* related to data quality. These were

- * Data Package Issues
- * Data Validation/Verification
- * Total Mercury in Water Data

The *Review* recommended:

- that all raw data provided by contract laboratories through the Interagency Agreements with the U.S. Department of Energy and the U. S. National Park Service should be obtained and maintained on file at EPA,
- validate or verify the quality of data generated,
- use flag fields to indicate validation/verification results, and
- document validation and verification criteria in metadata files or in a user's guide.
- recover additional sulfate data

As a result of the recommendations made in the *Quality of Science Review*, the SESD Office of Quality Assurance (OQA) and Region 4's Environmental Service Assistance Team (ESAT) conducted a data review of all available contractor acquired data for the Everglades Assessment Project.

In addition to the above recommendations, the OQA also conducted selected reviews of other raw data collected/analyzed by EPA staff and EPA's ESAT contractor. The goal of the audit of data quality was to provide a quantitative and qualitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data were of acceptable quality.

Data Collection Activities

The gathering of data for review was conducted in two phases. First, the OQA and ESAT Work Team conducted a preliminary review of the data submitted by the Florida International University (FIU) Southeast Environment Research Program (SERP) laboratory for sampling events conducted in 1993, 1994, 1995, and 1996. Randomly selected raw data packages were obtained by the OQA and ESAT Team during a visit to the SERP laboratory on March 12–14, 1997. Total and organic mercury raw data packages were also requested and received in March 1997, from Battelle Marine Sciences Laboratory (Battelle), Sequim, WA. AmTest Analytical Service, Inc., Seattle, WA, a subcontract laboratory for Battelle provided quality control (QC) split sample data for total nitrogen and phosphorus for the Marsh Cycle 3 sampling event. Raw data from AmTest were obtained in March 1998.

Since the Quality Assurance Project chemist participated in the ORD *Quality of Science Review*, and was part of the data review Team, an additional on-site visit was not made to the Battelle laboratory. The AmTest laboratory was not visited since only 26 samples were analyzed during the last sampling event of 1996.

After an initial assessment of the raw data packages, the second phase of the OQA/ESAT audit included two subsequent visits to the SERP on May 14–15, and October 14–15, 1997 to obtain additional raw data for the nine sampling events. The visits were necessary to fulfill the recommendation of *Quality of Science Review* Team that all raw data should be resident at Region 4 SESD and to allow the SERP personnel time to gather the large volume of raw data. A

third visit was made during June 1998 to review data stored in electronic format for methyl mercury at the SERP laboratory. During each visit members of the data review Team discussed the methodologies used and observed the SERP staff conducting the on-site analyses.

Data Review Guideline

Data were reviewed using data review practices employed by the OQA and the ESAT Team for regulatory and compliance monitoring programs with standard methodology. These practices included, but were not limited to, such items as sample collection, receipt, storage, checks of holding time, preparation, analysis, reporting, and all associated QC. Preparation checks included the use of blanks (reagent, digestion, lab and field blanks) for background correction, use of calibration standards and application of linear regression analysis of calibration curves for linearity, utilization of standard reference materials (SRMs) or performance evaluation samples, use of matrix spikes for accuracy, analysis of both field and laboratory duplicates for precision statements and determination of detection limits. Data packages also were reviewed against criteria addressed in the Data Quality Objectives (DQOs) and quality assurance requirements stated in Section 2.5; Data Quality Requirements in the EPA Project Research Plan; against SERP's Standard Operating Procedures (SOP) for Total and Methyl Mercury analyses; SERP's Comprehensive Quality Assurance Plan for the Mercury Laboratory dated 7/27/93, and subsequent revisions dated 6/14/94 and 4/18/96; and SERP's Methods Validation for Micromolar Concentrations of Total Nitrogen in Natural Water dated 4/25/96. The latter included total phosphorus and total organic carbon (TOC) SOPs. Because method development was a Project objective, the SERP staff expended considerable time in developing and refining methods and modifying the SOP's. These modifications were necessary as procedures were continually improved to enhance the quality of the data as the project moved from a research-orientation to a research-production environment. The same data review procedures were employed for the other participating contractor laboratories.

All data entries in the EPA database were checked against the raw data sheets from all laboratories for completeness and correctness. Relatively few transcription errors were observed considering the vast amount of data provided. Corrections were provided to the Project Leader.

Data Review Qualifiers

Reported data that did not satisfy all the criteria specified in the **Data Quality Review Guidelines** were qualified with appropriate codes. Each parameter that has data qualifier codes assigned has remarks added to assist the reader in understanding the code and the reason(s) for the qualifier or data flag. A list of qualifier codes accompany each parameter or group of similar parameters. The codes were:

<u>Code</u>	<u>Definition of analytical data qualifiers</u>
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<i>NR</i>	A “NR” Qualifier Code indicates that these data were not reviewed, since raw data were not available from the laboratory. In these cases, EPA data reviewers were not able to reconstruct the QC and analytical activities.
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“U”	The analyte was analyzed for but not detected. The value preceding the “U” is the “minimum quantitation limit (MQL)”.
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***Minimum Quantitation Limit (MQL) – Every sample has a concentration level below which the variance of the results for a particular analyte (element or compound) exceeds the acceptable quality control criteria. This level is the MQL and is reported as the value preceding the “U”. The MQL is determined from sample size, dilution required, and instrument sensitivity. The value often varies from analyte to analyte within a sample. Analytes are often detected at levels below the MQL and are reported as estimated values (J). Generally, analytes identified below the MQL will only be reported if concentration is greater than one tenth of the MQL.

“J”	The identification of the analyte is acceptable for use, but certain QC criteria were not satisfied.
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***Estimated Value--Every sample analysis has quality control criteria associated with the quantitative data which have been established based on similar analyses. When these criteria are exceeded, the value for that analyte or similar analytes is flagged. Examples are:

- (1) calculated values were below or above an appropriate linear range
- (2) calculated values were below the MDL or PQL of an analyte
- (3) analytical holding times for analysis were exceeded
- (4) surrogate recovery limits were exceeded
- (5) some QC criteria were not documented or followed as specified in the laboratory’s SOP or requirements necessary for confirmation were not met.

“A”	The analyte was analyzed in replicate. The value preceding the "A" is an "average value" of the replicates.
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***Average Value--Samples were often analyzed in replicate (usually in duplicate). Aliquots of the same sample were analyzed and the values are averaged. Sometimes replicate samples were analyzed and the values were reported as an average.

Specific data qualifier codes and explanations are provided with each constituent by media and by cycle and the associated data.

Summary of Data Review Findings

Summary results are presented for each constituent by media and by sampling cycle that data qualifier codes were assigned. Applicable recommendations are included. If there were no qualifying codes assigned, the data met the data quality review guidelines used to evaluate the data. Primary and secondary laboratories were used for sample analysis. The primary laboratory was the lead laboratory for the analysis with the secondary laboratory providing QA/QC on duplicate and split samples. The goal was to have QA/QC samples for about 10 percent of the total number of samples analyzed so the secondary laboratory had a significantly lower sample load.

1. Total and Organic Mercury in Soil/Sediment and Water by Battelle

Battelle served as the primary laboratory for methyl mercury in water and provided backup QC for total mercury in water splits/duplicates throughout the study and methyl mercury in soil/sediment after the Sept. 93 Canal sampling. The Battelle total and methyl mercury data for water and soils were reviewed for accuracy and compliance according to the same criteria used for SERP total and methyl mercury analyses. Linear regression was checked using the standards from the calibration curve. Quality control check samples were evaluated for recovery of the analyte from spiked samples and relative percent difference of duplicate samples. The final results were checked to ensure that the results were converted accurately from the instrument with the appropriate units. For example, the results for soil samples are converted from pg/ml to ng/g. Less than 5 percent of the methyl mercury samples for water were flagged "J" due to the quality control checks being outside of the acceptable limits: matrix spikes outside DQR limits (70 percent to 130 percent), duplicate samples results relative percent difference greater than 30 percent, or the calibration curve correlation coefficient less than 0.995.

After May 94, Battelle switched from an extraction to a steam distillation separation for soil/sediment samples. Matrix spikes were conducted and recoveries were acceptable. Duplicate splits with SERP were comparable with Battelle reporting values that tended to be higher than the SERP data. It has been reported that steam distillation could produce a methyl mercury artifact in samples containing elevated concentrations of total organic carbon (TOC) and total mercury (Hintelmann 1997). However, another study (Bloom 1997) using Everglades water and peat indicated this artifact would not be significant in Everglades samples. Methods for measuring ultra-trace level total and methyl mercury concentrations in water and soil/sediment are in the research phase. There currently is no standard EPA method for these constituents at these concentrations. Therefore, Battelle QA/QC soil/sediment data after May 94 should not be used solely in the establishing trends or environmental standards unless additional collaborative data are available to substantiate these original values

2. Total Mercury in Water by SERP

SERP served as the primary laboratory for the approximately 900 total mercury samples in water. These data were reviewed and validated. The September 1993 Canal and April '94 transect data for total mercury were flagged as "NR," not reviewed. The reason was the raw data were unavailable for review from the laboratory.

Data also were reviewed against QC checks EPA considered as good laboratory practices for regulatory or compliance monitoring programs with standard EPA methods. An independent stock standard prepared from another source to verify the initial calibration was not included in the analysis, but it was not part of SERP's SOP. The lack of this independent calibration check would not change the values obtained but would have strengthened the quality of the data. However, no data were flagged because SERP followed its SOP and the independent stock standard was not part of the initial QA plan reviewed by EPA. The independent stock solution will be added to future sample analyses.

The SERP data prior to May 1996 did not include a matrix spike. The matrix spike strengthens the data in that it shows that the analyte is actually being recovered during the digestion of the samples. According to SERP CompQAP, the accuracy of the matrix spike should be between 90–110 percent recovery or the sample analyses must be repeated. In May 1996, the data includes a water spike at 2 ng/l. Six of sixteen data sets had recoveries ranging from 83–122 percent with an average for all sets of 103 percent. In September 1996, the data included a sample (matrix) spike at 2 ng/l with 9 of 17 data sets having recoveries of 49–138 percent. The average percent recovery of this matrix spike for all 17 data sets was 94 percent recovery. However, none of the samples analyzed with the spike recoveries outside of SERP's stated performance limits were re-analyzed.

Although reagent blanks were analyzed, the sample results did not include a consistent reagent blank correction prior to May 1996. Just prior to the May 1996 sampling event, the SERP staff instituted a correction method that accounted for the background contribution from reagents and glassware. Correction for any contribution by the reagents was made utilizing varying concentrations of the reagents added to mercury free water and calculating the response due to the reagents using linear regression. Data previous to May 1996, were corrected for any reagent contribution by using an average value (0.5 ppt) for the reagent blank correction. The reagent blank corrects for any contamination due to the reagents and could alter the result at the lower concentrations if the contribution was significant. Since raw data for the first two sampling cycles were not available for review, a statement could not be made about the quality of the data. However, the SERP staff did have an in house policy of checking for background contamination and if background contamination was determined to be significant, samples were to be re-analyzed. Recalculation of the data using a four-point curve and subtracting the reagent blank showed differences of as much as 1.0 ng/L in only 4 out of 552 cases prior to May 1996.

A detection limit for total mercury was established by SERP at 0.3 ng/L using the recommended procedure for establishing detection limits given in 40 CFR 136 Appendix B. A low-level 0.3 ppt standard was not analyzed to show this level could be achieved each day. To provide a day-by-day assessment of the method stability near the MDL, a practical quantitation limit (PQL) for total mercury was established by the OQA data review Team at 1 ppt., (three times the standard deviation of 21 readings from the 2 ppt spike and reagent blanks). Results below 1 ppt. should be used with caution, especially since the lowest calibration standard reported as analyzed during the study was 2.5 ppt. The precision for field duplicates below 1 ppt ranged from 0–118 percent relative standard deviation (% RSD equals the standard deviation for duplicates divided by the mean time 100) with an average of 28 percent. Based on the review findings, the total mercury data in water by SERP were assigned a "J" flag except for the September 1993 canal data assigned "NR".

The “J” flag indicates the data are acceptable for use, but did not satisfy certain QA/QC criteria. The SERP data below 1.0 ppt should not be used solely for setting regulatory limits based on field precision and blank correction.

QC data for total mercury in water from split sample QC data provided from the Battelle laboratory showed a positive bias compared with data submitted by the SERP. However, the bias between the laboratories diminished during the May and September 1996 sampling events. The quality of the total mercury data were strengthened in two ways: 1) the observed collaborating trends for split samples between the SERP and Battelle laboratories; and 2) consistent performance by SERP and Battelle was observed on performance evaluation samples supplied as unknowns by the Project Quality Assurance Chemist to each laboratory. (See Table 1). Continued performance evaluation corroboration is expected to improve as mercury methods and analytical procedures continue to be refined.

Table 1 Total Mercury in Water Performance Evaluation Data (ppt)				
Date of Analysis	P.E. Value	SERP	Battelle	EPA
05/12/96 WP 30 C1	0.98	1.44	1.51	1U
05/13/96 WP 30 C2	2.10	1.73	2.30	2.20
05/14/96 WP 30 C1	6.23	5.71	6.14	6.20
09/15/96 WP 33 C1	5.81	5.02	5.73	5.60A
09/18/96 WP 33 C1	2.71	2.21	2.87	2.30
09/19/96 WP 33 C1	10.16	8.87	10.40	10.00
09/20/96 WP 33 C1	1.16	1.34	1.26	1.0UA

3. Total Mercury in Periphyton by SERP

SERP was the primary laboratory for the periphyton samples. QC check samples (SRM) were analyzed by SERP with each set of total mercury in periphyton analyses to verify the accuracy of the calibration standards and validate the digestion method from an independent source. SERP's acceptable range for these check samples was 90–110 percent recovery of the true value of the sample (60 ng/g). In 6 out of 16 data sets, this percent recovery was not achieved. The range of recovery was from 68–135 percent. The average recovery was 101 percent for the 16 sets.

A reagent blank was included in the analyses, but was not used to correct for reagent contamination in the final calculation of the sample results. The reagent blank correction versus no reagent blank correction showed a considerable difference (130 percent RPD) in sample results

where peak heights were less than two times the peak height of the reagent blank. This impacted greater than 50 percent of the samples for April 1995 and May 1996, but only 10 percent of the samples in September 1996. These sample values should be recalculated to remove the contribution for the blank or the detection limits should be increased. A check standard of 500 ng/l prepared from the same source was used for verification. Therefore, all total mercury data for periphyton were given a "J" code. The data are acceptable for use, but did not satisfy certain QA/QC criteria. The FL DEP recommends percent recovery ranges of 75–125 percent for biological samples, rather than 90–110 percent. These changes would be implemented in future sample analyses.

4. Total Mercury in Soil/Sediment by SERP

EPA-SESD served as the primary laboratory and SERP as the secondary or QC laboratory. A soil SRM was analyzed by SERP with each set of total mercury in soil/sediment analyses to verify the accuracy of the calibration standards and validate the digestion method from an independent source. SERP's stated acceptable range for this check sample (60 ng/g) was 90–110 percent recovery of the true value. In the May of 1994 canal data, this check sample did not meet SERP's acceptance limits. A reagent blank was included in the analyses to correct for reagent contamination in the final calculation of the sample results in all the data except in the May 1995 canal data. The results for these data were "J" coded since the recoveries did not meet the SERP's stated limits. The check standard was the high standard, at 500 ng/l. The September 1995 marsh split samples were coded "NR" because raw data were not available for review. However, data compared favorably between EPA-SESD and SERP values on split samples. The average concentration reported for the splits for EPA was 117 ng/gm and for SERP 156 ng/gm with a average difference of 39.6 ng/gm. Both labs had comparable %RSD of 13.7 and 15.2, respectively.

5. Total Mercury in Fish by SERP

SERP was the primary laboratory for total mercury in fish analyses. Whole mosquitofish (*Gambusia*) were digested and analyzed for total mercury. When the recovery QC criteria for the SRM did not meet acceptance limits, the analysis could not be repeated because the entire fish was digested. SRMs were included within the analyses to verify the accuracy of the data during the course of the analytical runs. For the September 1993 canal data, and one data set at the end of September 1994, SRMs were not analyzed. SERP set acceptance limits of 90–110 percent recovery of the true value for the SRM. The true value of the oyster tissue SRM was 64 ng/g and that of the dorm standard (Dog fish) was 4640 ng/g. The average percent recovery of the SRM (oyster std.) in September 1994 was 248 percent, and in April 1995, 287 percent. With the 64 ng/g oyster standard, there was not an adequate detector response following dilution, which contributed to the large variances for percent recovery. Four factors contributed to the wider range of recovery in the samples. First, the 64 ng/g SRM used did not provide an adequate detector response following dilution. Therefore, subsequent samples were run using the 4,640 ng/g SRM. Second, the inherent variability in biological samples results in larger percent recovery ranges. The FL DEP recommends percent recovery ranges of 75–125 percent, rather than 90–110 percent. Third there might have been either an interference (effervescing due to CO₂ production) and/or fourth some of the SRM weights were documented incorrectly based on conversations with the analysts. Corrections for the elevated recoveries were not warranted due to the stated problems. SERP switched to the dorm

standard because of sample handling problems. The average percent recovery for the Marsh sampling events were 92 percent for the April 1995 (range 77–99 percent), 98 percent for May 1996 (range 45–129 percent), and 80 percent in September 1996 marsh (range 45–100 percent).

Reagent blanks were included in the analyses, but were not used to correct for reagent contamination in the final calculation of the sample results. Reagent or glassware contribution in the blank impacted 110 samples analyzed from September 1994 to 1996. These sample values should be recalculated or the detection limits raised. Reagent blanks were not analyzed for 46 samples in September 1995 and 16 samples in September 1996. These data (172 of 704) were “J” flagged for no reagent blank correction. Matrix spikes were not analyzed because of the recognized difficulty to get a homogenous spike and the whole fish was used.

6. Organic Mercury in Soil/Sediment and Water by SERP

SERP served as the QA/QC laboratory for the Sept. ‘93 samples and as the primary laboratory for organic mercury in soil/sediment after Sept. ‘93. Battelle served as the primary laboratory for Sept. ‘93 but became the QC laboratory for solid/sediment duplicates/splits after this date. Samples and matrix spikes were analyzed in duplicate and results were corrected for recovery based on the matrix spike. SERP’s policy in place during the time period of 1993–1996 was to store the electronic copies of the methyl/ethyl mercury chromatograms. No hard copies of the GC chromatograms were stored. Electronic chromatograms were only available for Sept. ‘96 for review. Selected analytical runs (electronic copies) were reviewed by the Team during the June 1998 visit to SERP. The Team was able to confirm qualitative and quantitative steps taken by the analysts for the selected data (soil/sediment) sets reviewed. Split water samples with the Battelle laboratory showed acceptable agreement between the field replicates for water samples even though the methods were different. The comparison for soil/sediment samples analyzed by both laboratories showed SERP data having lower average concentration (0.63 ng/gm) from samples collected at the same site than the Battelle average (0.96 ng/gm). Table 2 lists the comparison for the methyl mercury data between the two laboratories. There were some Canal samples that SERP had much higher concentrations than data reported by Battelle. This would indicate if there were a artifact for the distillation procedure it was not a consistent phenomenon. None of these data were qualified.

Table 2 Precision Data for Methyl Mercury			
Parameter	Mean	%RSD	n
Methyl Mercury – (Battelle) H ₂ O ppt	0.408 ^a (0.39) ^b	14.68 (14.9)	68 (21)
Methyl Mercury – (SERP) H ₂ O ppt	0.21 ^b	33.7	21
Methyl Mercury – (Battelle) Soil ng/gm	0.96 ^c	-	62
Methyl Mercury – (SERP) Soil ng/gm	0.6 ^c	-	62

a = mean of duplicate pairs

b = mean of duplicate pair from same distribution

c = average concentration for samples analyzed by the respective laboratory from the same location.

7. Total Phosphorus by SERP

The total phosphorus data in soil and water were reviewed for accuracy and compliance with the SERP SOP. SERP followed the procedures as outlined in their SOP with some documentation deviations. The laboratory did deviate from EPA's common laboratory practices in preparing the calibration curve. SERP ran a five-point calibration curve and if the correlation coefficient for this curve was greater than 0.995, indicating good linearity, the curve was recalculated as a two-point curve using the high standard and the origin. Values were recalculated by the review Team using all four points and there was no significant difference in the SERP reported values and the EPA calculated results. SERP determined a MDL of 0.6 $\mu\text{g/L}$ using Appendix B to Part 136 of 40 CFR. A MDL of 1.4 $\mu\text{g/L}$ was calculated by the OQA/ESAT Team from blanks and the lowest standard analyzed over a period of time, which corresponds well with the SERP MDL. SERP's practical quantitation limit (PQL) was stated to be 1.8–3.0 $\mu\text{g/L}$ or 3–5 times the MDL. There were nine water values that had concentrations between 1.8–3.0 $\mu\text{g/L}$ and one value below the stated PQL. All soil sample results were well above the calculated PQL 2.2 $\mu\text{g/gm}$, and no detection limits were changed.

Total phosphorus in water precision data from field replicates collected during the study from the canals and marsh show an average %RSD of 16.7 for the concentration range of 1.3–361 $\mu\text{g/L}$. Total phosphorus in soil/sediment precision data from field replicates from the canals and marsh show an average %RSD of 13.5 for the concentration range of 44–2452 $\mu\text{g/gm}$.

Split sample data between SERP and AmTest for the Sept. '96 sampling event showed acceptable agreement between the two laboratories. AmTest reported a MDL of 5.0 $\mu\text{g/L}$ as compared to a lower MDL of 0.6 $\mu\text{g/L}$ for SERP. No data were qualified.

8. Total Organic Carbon by SERP

Data obtained for TOC were reported from an instrument that operated in the concentration only mode. The output of the instrument was in concentration units that were entered directly into the spreadsheet. It was not possible to check the actual calculations used to generate the results for this parameter. Calibration curves and standards were checked and found to be in order. Therefore, the TOC data were not qualified.

9. Total Nitrogen Data for Water by SERP and AmTest

SERP total nitrogen analyses (TN) were performed using an experimental method developed with a ANTEK Model 7000N elemental analyzer by direct aqueous injection of the samples. Results were calculated using a 2.0 mg/L KNO_3 standard. No SRM nor additional standards such as glycine, urea or another stock source were analyzed during the analytical run. Since this was a direct injection a reagent blank was not necessary. Raw data for quality control split samples from AmTest were reviewed. Comparison of data between SERP and AmTest showed SERP values to average 0.33 mg/L higher. However, the SERP method measured total nitrogen

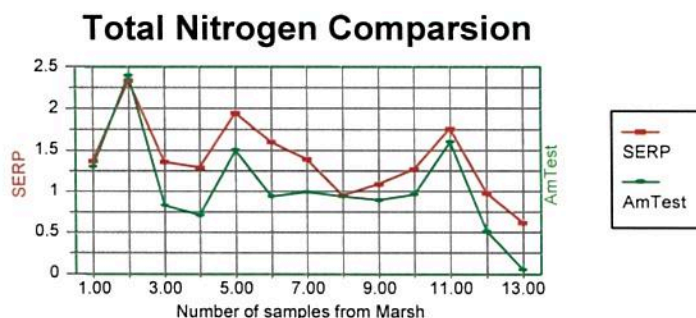
and AmTest measured total Kjeldahl nitrogen (TKN). The results for AmTest would be lower since nitrogen as nitrate-nitrite would not be determined but would be included in the SERP data. The AmTest nitrogen data should be reported as TKN instead of TN. No SERP TN data were qualified. The AmTest data were qualified based on reporting as TN instead of TKN.

10. Alkaline Phosphatase Data by ESAT

The Data Review Team has reviewed all the water alkaline phosphatase data. Comparison of data for the May and September 1996, sampling events showed a difference in the fluorescence readings of the standard curves for the 2.5, 5, and 10 micromolar (uM) methylfluorescein standards. The May standards appear to be approximately 1.5 times higher than the corresponding standards analyzed in September. Examination of the raw data showed the calibration curves for the analysis of both sampling events to be linear and recalculation of the curves by the data reviewer produced linear curves with correlation coefficients all greater than 0.990. The data reviewer was also able to reproduce the results for a selected random sampling of the samples for these sampling events. This would indicate that the calibration procedure and actual analysis of the data was performed correctly. It was not possible to compare samples analyzed in May and September to determine if the samples exhibited higher fluorescence in May, since there was no way to determine which sites, if any, were the same, or whether there should be a comparison. The method blanks, prepared daily from the methylfluoresceinphosphate substrate rather than the methyl fluorescein, were observed to see if the fluorescence readings for them were comparable between the May and September sampling events. Except for the method blank for the first analytical run in September, the fluorescence of the method blanks were reasonably consistent during all analytical runs in both May and September and compared quite well. The fluorescence reading for the method blank for the first analytical run in September is approximately 3 to 4 times the fluorescence readings for the other analytical runs in both May and September. An interview with the analyst was conducted. The age of the standard used to calibrate the Shimadzu Spectrofluorophotometer was a possible reason for the elevated May results. The only quality control standard analyzed, however, was the high standard (10 uM) from the calibration curve, which always gave better than 90 percent recovery.

The difference in the fluorescence readings in May and those in September '96 could be explained by the use of an old standard or more likely explained by possible changes in the Shimadzu instrument. Raw data were obtained from SERP for alkaline phosphatase in other similar samples analyzed just before, during and after the

May 1996 sampling event. These data showed similar fluorescence readings for the standards. There does not appear to be a practical way to recalculate the curves from the May sampling event so these samples match the curves from other sampling events, as stated above. It is not



recommended that a factor be used to make the curve fit other data. Such a procedure would not be scientifically defensible. Therefore, the Team concluded that the May 1996 alkaline phosphatase data (123 samples) are highly questionable and recommends that the data be rejected and not reported. EAB should delete the May 1996 data from the database to avoid any misuse at a later date.

11. Sulfide in Water by ESAT

The EPA SESD/ESAT laboratory was the primary laboratory for total sulfide in water analyses. EPA records show that sulfide samples were collected for September 1995 sampling event. However, the method used for sulfide analysis during the sampling event was not followed as written. Samples were not mixed properly prior to adding the color developing reagent. This would cause the values to have a negative bias. The OQA Project QA chemist upon learning of the sampling handling deviation after debriefing the analyst, recommended in writing to the EAB Project Leader that the sulfide data be rejected. For this reason, 123 sulfide data points for the September 1995 marsh cycle were rejected and not reported.

12. Sulfate in Water by EPA-SESD

EPA-SESD served as the primary laboratory for sulfate analyses. Analysis of water samples were conducted using the turbidimetric method based on Method 375.4 during the period from Sept. '93 - Sept 95. Starting in May '96 an ion chromatography (IC) Method 300 was used to provide lower detection limits better recoveries for spiked water samples. EPA-SESD policy is to report all results less than the lowest nonzero calibration standard as below detection (flag data with a "U". The detection limit changed over the course of the sampling program. A 5.0 mg/L or "5U" reported detection limit was used for the period of Sept. '93 - Sept. '94. In May 1995, the detection limit was lowered to 2.0 mg/L or reported as "2U" to provide additional data except for a couple of samples where the detection limit was 1.0 mg/L. A review of the %RSD showed that the variability was generally less than 8 %RSD indicating excellent precision and did not show the typical degradation of precision as the detection limit was approached. This indicated the laboratory was producing valid results before the declared detection limits and data could be reported at a lower level without compromise. The ion chromatograph method was commenced in May 1996, which allowed for reporting data down to 0.5 mg/L. Since many Marsh samples have concentrations below 0.5 mg/L a lower detection limit is needed for future studies to give added information for spatial display of the sulfate data.

13. Conclusions

The South Florida Everglades Ecosystem Assessment Project data set was reviewed against the Project DQOs, requirements defined in the Project Study Plan, each of the four laboratories SOPs and QC practices, and additional OQA procedures typically used for regulatory and compliance program reviews. Each individual datum was verified and validated. Over 20,425 measurements were made on samples analyzed by 4 laboratories for 20 constituents sampled in 5 media at about 200 canal sites and 550 marsh sites during the 9 field sampling events over the 10,000 km² area in South Florida. Included in these measurement were 7 structures sampled on a

bi-weekly basis from February 94 thru February 97. The data that have been qualified after this rigorous review are:

- “J” – Soil/sediment methyl mercury (5%) for the secondary laboratory
- “NR” – Water total mercury for September 1993 Canal samples and April ‘94 transect data for primary laboratory
- “J” – Water total mercury, excluding September 1993 Canal, for primary laboratory.
- “J” – Periphyton total mercury for primary laboratory
- “J” – Soil/sediment total mercury for May 1994, 1995 Canal cycles and May 1996 marsh samples for secondary laboratory
- “NR” – Soil total mercury for September 1995 marsh split samples for secondary laboratory
- “J” – Mosquitofish total mercury for very low mercury concentration fish and SRM for primary laboratory
- “J” – Total nitrogen for the secondary laboratory for Sept. ‘96 marsh samples
- Reject – Water alkaline phosphatase activity for 123 samples for May 1996 marsh cycle from the primary laboratory
- Reject – Water sulfide for 123 samples for the September 1995 marsh cycle from the primary laboratory.

This *Summary of Data Review Findings* report should be kept in perspective. The South Florida Ecosystem Assessment Project was a research and monitoring effort, not a regulatory compliance project. It developed and implemented new methods for rapidly analyzing a large sample load with ultra-trace level constituent concentrations. This rigorous review occurred over about a 2.5 year period, being initiated in 1995 and completed in 1998. Out of the over 20,425 measurements made over the four year period, only 15 percent of data was qualified. There were 1,325 points flagged “NR”- not reviewed because raw data were not available from the laboratory, 1,783 assigned a “J” flag - analyte identification was acceptable for use but certain QC criteria were not satisfied and 256 values rejected and not reported in the database.

The OQA finds that the data set satisfies the Project objectives and permits the assessment of trends and a characterization of status and extent of ecological condition in the South Florida Everglades ecosystem. Data qualified with a “J” code would not compromise the characterization and trend analysis or the Project objectives. “J” coded should not be used solely in the setting of environmental standards unless additional data are collected to substantiate these original values that have all supportive QC and documentation. These data can be used as part of the weight of evidence approach for establishing environmental standards.

This data set should provide an important baseline for assessing the current conditions of the Everglades ecosystem and for monitoring future trends in this condition. The results from this QA/QC Review have already been, and will continue to be, used to refine the QA/QC procedures in future Project monitoring efforts.